CONTENTS	
	Page
ACKNOWLEDGEMENTS	iii
ABSTRACT (English)	٧
ABSTRACT (Thai)	vii
LIST OF TABLES	XV
LIST OF ILLUSTRATIONS	xvii
LIST OF SCHEMES	xxiv
ABBREVIATIONS	XXV
CHAPTER 1 FIBRE SPINNING (with Special Emphasis on MELT SPINNING)	1
1.1 Introduction	1
1.1.1 Fibres	1
1.1.2 Manufacturing Methods	1
1.1.2.1 Spinning of Fibres	2
1.2 Melt Spinning	8
1.2.1 Development of Melt Spinning	8
1.2.2 Melting of the Polymer	9
1.2.3 The Spinnerette	10
1.2.4 Spinnability	12
1.2.5 Cooling and Drawing	13
1.3 Orientation and Crystallinity	17
1.3.1 The Arrangement of the Molecules in a Fibre	17
1.3.2 Crystalline Regions	19
1.3.3 Structure Formation During Spinning	20
1.3.3.1 Oriented Crystallization from the Melt	20

1.3.3.2 Development of High-Speed Spinning	22
1.4 Theoretical Variables in Fibre Formation	23
1.4.1 Number-Average Molecular Weight	24
1.4.2 Shear History of the Polymer	24
1.4.3 Shear in Spinnerette Capillary	24
1.4.4 Degree of Extension	25
1.4.5 Effective Time of Crystallization	25
1.4.6 Rate of Crystallization	25
1.4.7 Effective Temperature of Crystallization	26
1.4.8 Draw Ratio	26
1.4.9 Rate of Drawing	26
1.4.10 Actual Drawing Temperature	27
1.5 Aims of this Study	27
CHAPTER 2 EXPERIMENTAL METHODS	29
2.1 Small-Scale Fibre Melt Spinning	29
2.2 Polymer Characterisation and Fibre Testing	34
2.2.1 Instruments Used	34
2.2.2 Instrumental Methods	34
2.2.1.1 Infrared Spectroscopy (IR)	35
2.2.2.2 Nuclear Magnetic Resonance Spectroscopy	
(¹ H-NMR and ¹³ C-NMR)	37
2.2.2.3 Differential Scanning Calorimetry (DSC)	38
2.2.2.4 Thermogravimetry (TG)	40
2.2.2.5 Gel Permeation Chromatography (GPC)	42
2.2.2.6 Dilute-Solution Viscometry	47
2.2.2.7 Mechanical (Tensile) Testing	50

CHAPTER 3 MELT SPINNING STUDIES ON A MODEL POLYESTER:

POLY(E-CAPROLACTONE)	54
3.1 Introduction	54
3.2 Poly(ε-caprolactone)	55
3.3 Polymer Characterisation	57
3.3.1 Experimental Methods	57
3.3.2 Results	58
3.3.2.1 Molecular Weight Averages	58
3.3.2.2 Thermal Properties	61
3.3.2.3 Melt Flow Properties	65
3.4 Melt Spinning	66
3.4.1 Practical Considerations	66
3.4.2 Pre-Formed Rod Preparation	67
3.4.3 Fibre Spinning	70
3.4.3.1 Set-up and Procedure	70
3.4.3.2 Effects of Processing Variables	71
3.4.3.3 On-line Structural Development	78
3.5 Fibre Testing - Mechanical Properties	79
3.6 General Conclusions	81
CHAPTER 4 SYNTHESIS AND CHARACTERISATION OF COPOLYMERS AND	85
TERPOLYMERS OF L-LACTIDE, &-CAPROLACTONE AND GLYCOLI	DE
4.1 Chemicals and Instruments	85
4.1.1 Chemicals	85
4.1.2 Instruments	87
4.2 Monomer Preparation and Purification	88

4.2.1 L-lactide and Glycolide	88
4.2.1.1 Purity Analysis of L-Lactide and Glycolide	90
4.2.2 ε-Caprolactone	92
4.3 Homo-, Co-, and Terpolymer Syntheses	93
4.3.1 Poly(L-lactide) Homopolymer	93
4.3.2 Poly(L-lactide-co-ε-caprolactone) Random Copolymer	94
4.3.3 Poly(L-lactide-co-ε-caprolactone-co-glycolide) Random	
Terpolymers	95
4.3.4 Poly(L-lactide-co-ε-caprolactone-co-glycolide)	
Triblock Terpolymer	96
4.4 Polymer Characterisation	99
4.4.1 Fourier - Transform Infrared Spectroscopy (FT-IR)	99
4.4.2 Nuclear Magnetic Resonance Spectroscopy	105
(¹ H-NMR and ¹³ C-NMR)	
4.4.2.1 Proton Nuclear Magnetic Resonance	
Spectroscopy (¹ H-NMR)	105
4.4.2.2 Carbon-13 Nuclear Magnetic Resonance	
Spectroscopy (¹³ C-NMR)	111
4.4.3 Thermal Analysis	117
4.4.3.1 Differential Scanning Calorimetry (DSC)	117
4.4.3.2 Thermogravimetry (TG)	123
4.4.4 Molecular Weight Determination	127
4.4.4.1 Dilute-Solution Viscometry	127
4.4.4.2 Gel Permeation Chromatography (GPC)	128

CHAPTER 5 FIBRE PROCESSING AND TESTING OF THE P(LCG) TERPOLYMERS 132

5.1 Processing Operation	132
5.1.1 Spinning Conditions	132
5.1.2 Off-line Hot-Drawing	135
5.1.3 Annealing	137
5.2 Fibre Morphology	138
5.2.1 As-spun Morphology	138
5.2.2 Effects of Hot-drawing and Annealing	139
5.3 Fibre Testing - Mechanical Properties	143
5.3.1 Test Parameters and Conditions	143
5.3.2 Main Conclusions	144
CHAPTER 6 X-RAY DIFFRACTION MEASUREMENTS ON THE P(LC) COPOLYMER	
FIBRES A CASE STUDY	153
6.1 P(LC) Random Copolymer – Fibre Processing	154
6.2 X-Ray Diffraction	157
6.2.1 Introduction	157
6.2.2. Description of Orientation [67]	159
6.2.3 Experimental Procedure and Diffraction Patterns	163
6.2.4 Molecular Orientation Parameters	166
6.3 Concluding Remarks	174
CHAPTER 7 MAIN CONCLUSIONS	176
7.1 Molecular Design	176
7.2 Polymer Synthesis	177
7.3 Polymer Characterisation	177

7.4 Fibre Processing	181
7.5 Random Versus Triblock Terpolymers	183
SUGGESTIONS FOR FURTHER WORK	186
REFERENCES	188
VITA	192
APPENDIX (Supporting Papers)	193

LIST OF TABLES

Tab	le	Page
1.1	Comparison of the three principal methods of fibre spinning	4
2.1	Instruments used in this research project	34
2.2	Dilute-solution viscosity terms currently in use	48
3.1	Comparison of the various molecular weight values obtained for the	
	PCL beads used in this work	59
3.2	Summary of the effects of some processing variables on the as-spun	
	monofilament fibre diameter. (Spinnerette diameter= 2.0 mm,	
	spinnerette to cooling bath air gap = 4.00 cm)	73
3.3	Effect of spinnerette hole size on PCL fibre diameter at different ram	
	speeds. (Temperature = 85°C, take-up speed = 0.60 m/min, spinnerette	
	to cooling bath air gap = 4.00 cm)	75
3.4	Effect of air gap on PCL fibre diameter under otherwise constant	
	conditions. (Temperature = 85°C, spinnerette diameter = 2.0 mm,	
	ram speed = 2.0 mm/min, take-up speed = 0.6 m/min)	76
3.5	Effect of stainless steel wire mesh on PCL fibre diameter under	
	otherwise constant conditions. (Temperature = 85°C, spinnerette	
	diameter = 2.0 mm, ram speed = 2.0 mm/min, take-up speed = 0.6 m/min)	77
3.6	Variations in PCL fibre diameter and % crystallinity along the filament	
	line during melt spinning. (Temperature = 85°C, spinnerette	
	diameter =2.0 mm, ram speed = 2.0 mm/min, take-up speed = 0.6 m/min)	79
4.1	Chemicals used in this research project	86
4.2	Instruments used in this research project	87
4.3	Conditions used in the random terpolymerisations of L-lactide,	
	s-caprolactone and alveolide	05

4.4	Peak assignments and vibrational frequencies in the homo-, co- and	
	terpolymer IR spectra.	104
4.5	Comparison of the initial co- and termonomer feeds with the final	
	co-, and terpolymer compositions.	110
4.6	DSC transition temperatures and heats of melting of the homo-,	
	co-, and terpolymers.	122
4.7	TG thermal degradation ranges for the polymer products studied.	127
4.8	Molecular weight data relating to the polymer products.	131
5.1	Processing conditions used for melt spinning of the P(LCG) terpolymers.	133
5.2	Fibre diameters and on-line draw ratios of the as-spun terpolymer fibres.	134
5.3	Conditions used in the off-line hot-drawing of the P(LCG) terpolymer fibres.	136
5.4	Annealing conditions used for the terpolymer fibres following hot-drawing.	137
5.5	DSC melting temperatures, T_m , and heats of melting, ΔH_m , for the polymer	
	fibres at various stages of processing.	142
5.6	Comparison of the mechanical properties of the PL homopolymer and	
	P(LCG) random and triblock terpolymer fibres.	152
6.1	Mechanical property values of the series of P(LC) fibres in Fig. 6.3 above.	156
6.2.	Spherical harmonic coefficients evaluated using $I(\alpha)$ at $Q = 1.18 \text{ Å}^{-1}$ for the	
	P(LC) copolymer fibres at various draw ratios.	173

LIST OF ILLUSTRATIONS

Figure		Page
1.1	Idealized diagrams of various yarn structures	3
1.2	Typical cross-sections of fibres produced by the three different spinning	
	processes	6
1.3	Schematic diagrams of the three principal types of fibre spinning	7
1.4	Correlation between the main factors governing the melt spinning	
	process	8
1.5	Typical spinnerettes used in melt spinning	12
1.6	Schematic diagram of a typical fibre drawing process	14
1.7	Schematic diagrams of the production processes used for making	
	poly(ethylene terephthalate) (PET) yarn	15
1.8	Random arrangement of molecules in a fibre	18
1.9	Orientation of molecules in a fibre after drawing	18
1.10	Diagrams representing both ordered (crystalline) and random	
	(amorphous) regions in the same fibre. (Lower diagram represents	
	a lower degree of crystallinity than the upper. Note that in either	
	case the longest molecules can pass from one crystalline region	
	right through an amorphous region to another crystalline region.)	19
1.11	Change of fibre structure in high-speed spinning	23
2.1	Schematic diagram of the small-scale melt spinning apparatus.	29
2.2	Photograph of the small-scale melt spinning apparatus	30
2.3	Photograph showing some of the various accessories used in	
	the small-scale melt spinning apparatus	31
2.4	Schematic diagram of the compression	32
2.5	FT-IR spectra of isotactic polystyrene in the 640 to 840 cm ⁻¹ region	36

2.6	A typical non-isothermal TG thermogram for a polymer showing	
	the various reaction parameters derived from the curve	40
2.7	GPC elution curve showing schematically the range of elution volumes	
	which are valid for a particular column	44
2.8	Universal GPC calibration curve for several polymers in	
	tetrahydrofuran as solvent at 30°C	45
2.9	Diagrams of (a) an Ostwald U-tube viscometer, (b) a Ubbelohde	
	suspended-level viscometer, and (c) a modified Ubbelohde	
	viscometer with a larger reservoir bulb for dilutions	48
2.10	Photograph of the Lloyds LRX+ Universal Testing Machine used for	
	fibre tensile testing	51
2.11	Close-up photograph of the bollard grips showing the fibre sample	
	mounted in position at the start of a test	51
3.1	GPC curve of the PCL beads	59
3.2	Zimm plot of the PCL beads from light scattering	60
3.3	Reduced (η_{red}) and inherent (η_{inh}) viscosity-concentration plots for	
	the PCL beads in benzene as solvent at 25°C	60
3.4	Reduced (η_{red}) and inherent (η_{inh}) viscosity-concentration plots for	
	the PCL beads in benzene as solvent at 30°C	61
3.5	DSC heating curves showing the melting peaks of (a) the PCL beads,	
	(b) an as-spun fibre and (c) an off-line drawn (x25) fibre	62
	(Heating rate = 5 °C/min)	
3.6	DSC cooling curves showing the PCL crystallization peaks at cooling	
	rates of (a) 1 °C min ⁻¹ (b) 2 °C min ⁻¹ (c) 5 °C min ⁻¹ and (d) 10 °C min ⁻¹	63
3.7	TG curve showing the thermal decomposition (weight loss) range	
	of the PCL beads. (Heating rate = 20°C min ⁻¹)	64

3.8	Graph showing the variation in melt flow index (MFI) with temperature	
	under constant load for the PCL beads. (Load = 2.16 kg, pressure ≈ 300 kF	a)66
3.9	The various accessories used in pre-formed rod preparation	68
3.10	The assembled pre-forming cylinder used for making PCL rods	69
3.11	The assembled extrusion cylinder ready for fibre spinning	71
3.12	Diagram showing the 4 positions along the filament line at which	
	samples were taken for studying on-line structural development	78
3.13	Stress-strain curves of the PCL fibres showing the effects of increasing	
	the off-line draw ratio (Off LDR) on tensile properties	80
3.14	Visualization of the sequence of molecular rearrangement processes	
	which can occur during the melt spinning of a monofilament fibre	83
4.1	Apparatus used in the two-step preparation of L-lactide (or glycolide)	89
4.2	DSC curve of purified L-lactide	90
4.3	DSC curve of purified glycolide	90
4.4	Van't Hoff plot of the purity analysis data for the purified L-lactide	91
4.5	Van't Hoff plot of the purity analysis data for the purified glycolide	92
4.6	Reference infrared spectrum of poly(L-lactide), PL [60]	99
4.7	Reference infrared spectrum of poly(ε-caprolactone), PCL [61]	100
4.8	Reference infrared spectrum of polyglycolide, PG [62]	100
4.9	FT-IR spectrum of the synthesized poly(L-lactide), PL	101
4.10	FT-IR spectrum of the P(LC) 80:20 random copolymer	101
4.11	FT-IR spectrum of the P(LCG) 1 70:20:10 random terpolymer	102
4.12	FT-IR spectrum of the hydroxyl-terminated P(LC) 50:50 prepolymer	102
4.13	FT-IR spectrum of the P(LCG) 70:20:10 triblock terpolymer	103
4.14	60 MHz ¹ H-NMR spectrum of the PL homopolymer	106
4.15	300 MHz ¹ H-NMR spectrum of the P(LC) 80:20 random copolymer	107
4.16	60 MHz ¹ H-NMR spectrum of the P(LCG) 1 70 : 20 : 10 random terpolymer	107
4.17	60 MHz ¹ H-NMR spectrum of the P(LCG) 2 70 : 20 : 10 random terpolymer	108

4.18	60 MHz ¹ H-NMR spectrum of the P(LCG) 3 70:20:10 random terpolymer	108
4.19	60 MHz ¹ H-NMR spectrum of the hydroxyl-terminated P(LC) 50: 50	
	prepolymer	109
4.20	60 MHz ¹ H-NMR spectrum of the P(LCG) 70 : 20 : 10 triblock terpolymer	109
4.21	75 MHz ¹³ C-NMR spectrum of the PL homopolymer	111
4.22	75 MHz ¹³ C-NMR spectrum of the P(LC) 80 : 20 random copolymer	112
4.23	75 MHz ¹³ C-NMR spectrum of the P(LCG) 1 70:20:10 random	
	terpolymer	112
4.24	75 MHz ¹³ C-NMR spectrum of the hydroxyl-terminated P(LC)	
	50 : 50 prepolymer	113
4.25	75 MHz ¹³ C-NMR spectrum of the P(LCG) 70 : 20 : 10 triblock terpolymer	113
4.26	Expanded carbonyl region of the ¹³ C-NMR spectrum of the	
	PL homopolymer	114
4.27	Expanded carbonyl region of the ¹³ C-NMR spectrum of the	
	PCL homopolymer	114
4.28	Expanded carbonyl region of the ¹³ C-NMR spectrum of the P(LC)	
	80 : 20 random copolymer	115
4.29	Expanded carbonyl region of the ¹³ C-NMR spectrum of the	
	P(LCG)1 70:20:10 random terpolymer	115
4.30	Expanded carbonyl region of the ¹³ C-NMR spectrum of the	
	hydroxyl-terminated P(LC) 50 : 50 prepolymer	116
4.31	Expanded carbonyl region of the ¹³ C-NMR spectrum of the	
	P(LCG) 70 : 20 : 10 triblock terpolymer	116
4.32	DSC thermogram of the synthesized poly(L-lactide), PL	118
4.33	DSC thermogram of commercial poly(ε-caprolactone)	118
4.34	DSC thermogram of polyglycolide [35]	119
4.35	DSC thermogram of the P(LC) 80 : 20 random copolymer	110

4.36	DSC thermograms of the (a) P(LCG)1, (b) P(LCG)2 and	
	(c) P(LCG)3 70 : 20 : 10 random terpolymers	120
4.37	DSC thermogram of the hydroxyl-terminated P(LC) 50 : 50 prepolymer	120
4.38	DSC thermogram of the P(LCG) 70:20:10 triblock terpolymer	121
4.39	TG thermogram of the synthesized poly(L-lactide), PL	123
4.40	TG thermogram of commercial poly(ε-caprolactone)	124
4.41	TG thermogram of polyglycolide [62]	124
4.42	TG thermogram of the P(LC) 80: 20 random copolymer	125
4.43	TG thermograms of the P(LCG) 70 : 20 : 10 random terpolymers	125
4.44	TG thermograms of (a) the P(LC) 50: 50 prepolymer and (b) the P(LCG)	
	70:20:10 triblock terpolymer	126
4.45	GPC curve of the P(LC) 80 : 20 random copolymer	129
4.46	GPC curve of the P(LCG)1 70:20:10 random terpolymer	129
4.47	GPC curve of the P(LC) 50: 50 prepolymer	130
4.48	GPC curve of the P(LCG) 70: 20: 10 triblock terpolymer	130
5.1	Schematic arrangement used for off-line hot-drawing	135
5.2	DSC thermogram (heating) of the poly(L-lactide), PL, as-spun fibre	140
5.3	DSC thermograms (heating) of the as-spun (above) and	
	hot-drawn +annealed (below) P(LCG)1 random terpolymer fibres	140
5.4	DSC thermograms (heating) of the as-spun (above) and	
	hot-drawn +annealed (below) P(LCG)2 random terpolymer fibres	141
5.5	DSC thermograms (heating) of the as-spun (above), annealed (middle)	
	and hot-drawn +annealed (below) P(LCG)3 random terpolymer fibres	141
5.6	DSC thermograms (heating) of the as-spun (above) and	
	hot-drawn +annealed (below) P(LCG) triblock terpolymer fibres	142
5.7	Stress-extension curves of the poly(L-lactide) as-spun fibres	147
5.8	Stress-extension curves of the P(LCG)1 random terpolymer as-spun	
	(above) and hot-drawn + annealed (below) fibres	148

5.9	Stress-extension curves of the P(LCG)2 random terpolymer as-spun	
	(above) and hot-drawn + annealed (below) fibres	149
5.10	Stress-extension curves of the P(LCG)3 random terpolymer	
	as-spun (top) annealed (middle) and hot-drawn + annealed (bottom) fibres	150
5.11	Stress-extension curves of the P(LCG) triblock terpolymer as-spun	
	(above) and hot-drawn + annealed (below) fibres	151
6.1	DSC thermogram of the as-spun P(LC) random copolymer fibre	154
6.2	DSC thermograms of the as-spun P(LC) fibres annealed at 60°C for	
	different periods of time	155
6.3	Comparison of the stress-extension curves for a series of P(LC) fibres	
	hot-drawn at 65°C to various draw ratios (DR) before being annealed	
	at 65°C for 10 hours	156
6.4	Schematic diagram for X-ray diffraction from a semi-crystalline polymer	157
6.5	Wide angle X-ray scattering (WAXS) patterns of a drawn poly(ethylene	
	terlephthalate) fibre subjected to a series of processing operations [65]	158
6.6	Section through a polar probability plot of a uniaxial orientation	
	distribution [67]	162
6.7	Polar plots of the spherical harmonic functions P ₀ , P ₂ , P ₄ and P ₆ [67]	163
6.8	P(LC) copolymer fibre sample mounting for X-ray diffraction measurements	164
6.9	X-ray scattering patterns of the P(LC) copolymer fibres	165
6.10	Schematic diagrams of (a) the 3-circle X-ray diffractometer	
	and (b) the scattering geometry, reproduced from Reference [68]	168
6.11	Contour plots of the 2-D diffraction patterns of the P(LC) copolymer fibres	169
6.12	X-ray scattering intensity functions for the P(LC) copolymer fibre of	
	DR=8, as measured along the equatorial	170
6.13	X-ray scattering intensity functions for the P(LC) copolymer fibre of DR=8,	
	as measured along the meridian	170

6.14	X-ray scattering intensity functions for the as-spun P(LC) copolymer fibre	
	measured along both the equatorial (—)and the meridian ()	171
6.15	Scattering intensity profile for the P(LC) copolymer fibre of DR=8 at Q = 1.18 Å ⁻¹	172
7.1	Visualization of the sequence of molecular rearrangement processes	
	which can occur during the melt spinning of a monofilament fibre	185

LIST OF SCHEMES

Sche	emes	Page
4.1	Two-step preparation of the P(LCG) triblock terpolymer	98
	(a) First step, P(LC) prepolymer synthesis	
	(b) Second step, P(LCG) triblock terpolymer synthesis	
7.1	Cordination-insertion mechanism for the ring-opening	179
	polymerization of L-lactide using stannous octoate	
	as catalyst and diethylene glycol as initiator	

ABBREVIATIONS

T_c crystallisation temperature

T_g glass transition temperature

T_m melting temperature

IR infrared

FT-IR fourier-transform infrared

¹H-NMR proton nuclear magnetic resonance

¹³C-NMR carbon-13 nuclear magnetic resonance

DSC differential scanning callorimetry

TG thermogravimetry

GPC gel permeation chromatography

XRD X-ray diffraction

SAXS small angle X-ray scattering

WAXS wide angle X-ray scattering

DR draw ratio

Rh relative humidity

Fig. Figure

°C degrees Celcius

K degrees Kelvin

Mpa megapascal

Kgf Kilogram force

 μ m micrometre

min minute

hr hour

mg milligram

g gram

ml millilitre

mmol millimole

M molar

g/mol grams per mole

g/I grams per litre

MHz megahertz

 ΔH_{m} heat of melting

J/g joules per gram